Interpreting the Origins and Evolutions of Martian Basalts from Pyroxene Composition: II. Vibrational Spectroscopy of Clinopyroxenes and Terrestrial Basaltic Rocks

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Introduction. The Thermal Emission Spectrometer (TES) on the Mars Global Surveyor spacecraft will return thermal IR spectral data of martian surface materials for the purposes of geological mapping. Our goal is to quickly and accurately derive the compositions of martian basalts from these data once spectra of the martian surface are acquired. We are preparing to interpret these data by examining the spectral characteristics of pyroxenes (common minerals in mafic compositions) and igneous rocks. Pyroxenes ranging in composition from augite (clinopyroxene) to low-Ca orthopyroxene have been identified on the martian surface in studies of visible and near-infrared spectroscopic data [1-4]. If both ortho- and clinopyroxene are present in a rock, they may be used to establish pressure and temperature conditions of the melt. Laboratory spectroscopic studies of pyroxenes and pyroxene-bearing igneous rocks have been carried out in order to (1) characterize the spectral effects of compositional variations among pyroxenes, (2) establish the compositional differences detectable among individual pyroxene minerals using vibrational spectroscopy, and (3) determine whether or not pyroxene spectral features can be observed in the spectra of various mafic igneous rocks, and their quantitative abundance(s) calculated.

Sample preparation and procedure. Pure mineral samples were crushed and sieved to particle sizes between 710 μm and 1 mm. Rock samples are roughly hand-sized, and modal mineral abundances were determined by optical (thin section) analysis [5]. Thermal emission spectra were acquired and processed using the methods of [6] and [7].

Analytical Techniques. At thermal IR wavelengths, absorption features in a mineral spectrum are due to the characteristic stretching and bending vibrations of atoms in the crystal lattice. All minerals have unique vibrational signatures which may be identified in rock spectra and used for determining their relative abundances, thus providing vital petrologic information. Previous studies have shown that a linear deconvolution technique is valid for determining quantitative modal abundances in mineral mixtures [8] and martian meteorite samples [9]. This technique is based on the idea that the spectrum of a mixture of mineral grains or of a rock is equivalent to the sum of the spectra of the constituent minerals in proportion to the observed areal percentage of each mineral. In this study, two groups of mineral endmember spectra were used to deconvolve mafic rock spectra: a mafic suite, and a felsic (granitic) suite. After each analysis using the mafic suite, the felsic suite was used in a second analysis to show that felsic minerals alone could not provide equally good or better fits to the rock spectrum.

Results and Discussion. The shapes and number of absorption bands in the spectra of clinopyroxenes are clearly different than those of orthopyroxenes, serving to distinguish minerals of the two structural groups (Figure 1) [10]. Furthermore, we find that the minerals of the clinopyroxene solid solution series (diopside, augite, and hedenbergite) can also be distinguished on the basis of their spectral characteristics (Figure 2). In the 1200 - 800 cm^{-1} region, all three minerals display two broad groups of absorptions, one centered at approximately 1075 cm^{-1} and one around 900 cm^{-1}. The spectra of the pure endmembers diopside and hedenbergite contain an additional small yet distinctive feature at 1010 or 1000 cm^{-1}. This trough is not apparent in the spectrum of augite, suggesting that the changes in mineral structure (and vibrational character) with Mg/Fe substitution in intermediate compositions result in concealment of this feature in the spectrum. At longer wavelengths, from approximately 600 - 400 cm^{-1}, hedenbergite is clearly distinguishable from diopside and augite because there are only two low emissivity troughs, whereas in diopside and augite, there are typically three distinct troughs (peaks in reflectance). Band position is also correlated to composition in the clinopyroxene series. As clinopyroxene compositions move from diopside to hedenbergite (Mg to Fe), the positions of the band centers shift to longer wavelengths. For example, as mentioned above, diopside and hedenbergite have a similar small absorption that is located at 1010 cm^{-1} in diopside and at 1000 cm^{-1} in hedenbergite. These differences in band shape and band position allow discrimination between the three clinopyroxene minerals.

The ability to detect intra-mineral variations in composition is also important. If these distinctions can be made accurately and precisely from mineral spectra, and they can be discriminated in rock spectra, it may become possible to perform more complex analyses such as geothermometry on pyroxene-bearing rocks. While preliminary results suggest that some correlations related to Ca-content and Mg/Fe ratio are apparent in clinopyroxene spectra, more samples need to be studied to provide conclusive evidence.

Finally, we apply our current understanding of pyroxene spectra to the identification of pyroxenes in rock spectra. We obtained spectra of many igneous compositions, including a pair of basaltic andesites (samples 94-8 and 94-41). Figure 3 shows the spectra of plagioclase and clinopyroxene with the spectra of the rock samples and spectra produced by the linear deconvolution model.

Overall, the modal abundances calculated by the linear deconvolution algorithm were in very good agreement with the modes determined by optical analysis. The optically determined modes for both rocks were generally similar: ~70% plagioclase, ~15-20% clinopyroxene, ~5-7% olivine, and ~5% opaque minerals and minor phases. Errors in the optically-determined modes are estimated to be between 5-10% [5]. The linear deconvolution algorithm calculated the following modes from the rock spectra: 66%

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plagioclase, 28% pyroxene, and 6% olivine (sample 94-8); 74% plagioclase, 19% pyroxene, 1% olivine, and 5% serpentine (sample 94-41). All of the calculated modes lie within the error range of the optical modes. Augite provided the best fit to the clinopyroxene component in both cases, while a very small percentage of the pyroxene present was determined to be orthopyroxene, suggesting that lamellar opx may be present at optically small scales. The presence of serpentine in sample 94-41 was confirmed by review of the thin section analysis, in which serpentine was listed as an alteration product of olivine (hence the low olivine mode). Minor phases are difficult to detect, as described by [9]. The spectra produced using model-derived modes are shown in Figure 3. Spectral features of augite visibly contribute to the shape of the spectra of the basaltic samples. The model spectra are very good matches to the measured rock spectra, suggesting that the minerals used in the fit are in fact the correct minerals. Model results using the granitic endmember suite yielded poor fits to the rock spectra.

   Conclusion. Thermal IR spectra of pyroxenes display intermineral compositional variations. Absorption bands in pyroxene spectra provide a visible contribution to spectra of pyroxene-bearing rocks, and furthermore, allow for the determination of pyroxene composition in the complex spectra of basaltic rocks, where pyroxene modal abundances may be as low as 15-20%. In the future, the ability to accurately and precisely determine the compositions of pyroxenes within rocks may yield geothermometric information that could provide constraints on the origins of martian basalts. Correlation of basaltic compositions with stratigraphic data may then provide a global history of the evolution of basaltic volcanism on Mars.

   References. [1] ADAMS, J.B., *JGR*, 79, 4829-4836, 1974. [2] SINGER, R.B., *Lunar Planet. Sci.*, **XI**, 1048-1050, 1980. [3] SINGER, R.B. AND T.L. ROUSH, *Amer. Astron. Soc. Bull.*, **17**, 737, 1985. [4] MUSTARD, J.F., ETAL., *J. Geophys. Res.*, **98**, 3387-3400, 1993. [5] LEIGHTY, R. S., pers. comm., 1996. [6] HAMILTON, V. E., AND CHRISTENSEN, P. R., *LPSC XXVI*, 543-544, 1995. [7] RUFF, S. W., ET AL., *JGR, submitted,* 1996. [8] RAMSEY, M. R., Ph.D. dissertation, *Ariz. State Univ.*, 1996. [9] HAMILTON, V. E., ET AL., *JGR, submitted*, 1996. [10] HAMILTON, V. E., AND CHRISTENSEN, P. R., *LPSC XXVII*, 481-482, 1996.

Figure 1. Vibrational emission spectra of enstatite (opx) and augite (cpx). In all figures, the scale at top is in micrometers, and the vertical axis is emissivity, with spectra offset for clarity.

Figure 2. Emission spectra of clinopyroxenes.

Figure 3. Spectra of feldspar and pyroxene (at top) are shown with rock and model-derived spectra. Vertical lines correspond to augite absorption features apparent in the basalt spectra.